Consider Nanofiltration for Membrane Separations

Falling in between reverse osmosis and ultrafiltration, this method is finding growing applications in the CPI.

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The best known liquid-phase membrane processes are reverse osmosis (RO), ultrafiltration (UF), microfiltration (MF), dialysis, and electrodialysis (ED). However, over the past few years, a new membrane process called nanofiltration (NF) has emerged that promises to significantly widen the application of membranes in liquid-phase separations.

NF operating range

NF falls in between RO and UF in its separation characteristics (Figure 1). For example, RO membranes reject both sugars and salts, while UF types freely pass both solutes. NF membranes, on the other hand, retain sugars and certain multivalent salts (*e.g.*, $MgSO_4$), but pass substantial amounts of most monovalent salts (*e.g.*, NaCl).

Since low-molecular-weight salts are the ones mainly permeating the membrane, the osmotic pressure difference is much less than for an RO membrane. Thus, NF membranes require lower pressures (*e.g.*, 1.4 MPa/200 psi) than RO, which require pressures above 4 MPa (600 psig).

Although "leaky" RO membranes, made from cellulose acetate and yielding 10–80% salt rejections, have been available commercially for several years, it was not until thin-film composite NF membranes were developed that NF became a viable unit operation. Today, loose RO, low-pressure RO and ultra-osmosis membranes are all NF membranes. Some membranes designated as charged RO/UF also show similar properties and are classified here as NF membranes.

Membrane properties

Most NF membranes are multiple-layer thin-film composites of polymers. The active membrane layer usually consists of negatively charged chemical groups. NF membranes are believed to be porous with an average pore diameter of 2 nm. As a general rule, the nominal molecular weight cutoff ranges from 100–200 (Figure 2).

Salt rejection by NF membranes is mainly due to electrostatic interaction between the ions and the membrane. On the other hand, rejection of neutral species is by size, as in the rejection of sugars (glucose, sucrose, lactose), with typical rates of 90-98%. Properties and performance characteristics of some commercially available NF membranes are listed in Table 1.

NF membranes also show selectivity based on charge density of the ion. For ion-selective membranes with solutions containing different free ions, an unequal distribution of ions results across the membrane (transport rates change as ion concentrations change). This is known as the Donnan effect. For example, if the solution contains Na_2SO_4 and NaCl, and the membrane preferentially rejects SO_4^{-2} ions over Cl^-, the rejection of Cl^- decreases as the concentration of Na_2SO_4 increases. To maintain electroneutrality, the Na^+ also permeates the membrane. At high SO_4^{-2} concentrations, rejections can even be

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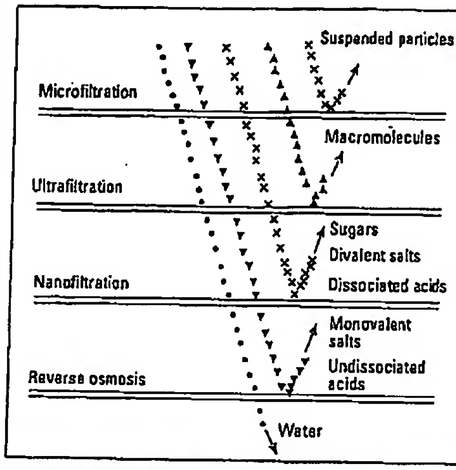

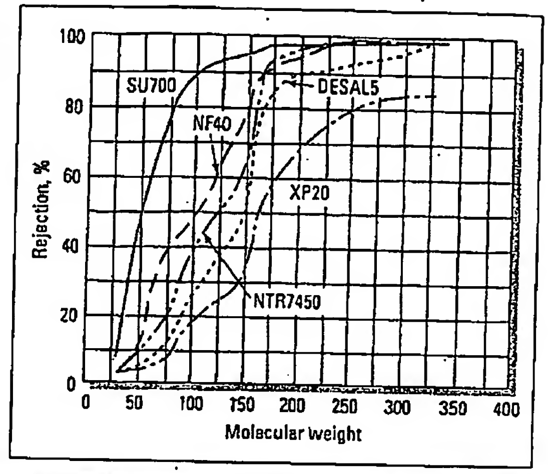

■ *Figure 1. (right) NF fulfills a new role in membrane separation processes.*

■ *Figure 2. (far right) For NF, the cutoff point ranges between a molecular weight of 100 to 200. Adapted from (22). Numbers refer to catalog items in the table, except for SU700, which is manufactured by Toray (Japan).*

Table 1. Properties and performance characteristics of some commercially available NF membranes.

Company and location	Membrane name	Active membrane layer*	Charge	Water permeability coefficient, L/m²/hr/MPa	NaCl Conc., %	NaCl Rej., %	$MgSO_4$ Conc., %	$MgSO_4$ Rej., %
Celfa, Germany	DCR-100	†	†	51.9	0.35	10	†	†
DDS Nakskob, Denmark	HC50	†	†	20.8	0.25	60	†	†
Desalination Systems Escondido, CA	Desal-5	†	†	47.1	0.1	50	0.1	96
Film-Tec (Dow) Minneapolis, MN	NF-40 NF-70 XP-20 XP-45	PA PA † †	Negative Negative † †	25.0 72.0 50.0 30.7	0.2 0.2 0.2 0.2	45 70 25 75	0.2 0.2 0.2 0.2	97 98 75 98
Kalle Germany	NF-PES10/PP60 NF-CA50/PET100	† †	† †	103.8 31.0	0.5 0.5	15 55	† †	† †
Membrane Products-Kiryat Weizmann Rehovot, Israel	MPT-10 MPT-20 MPT-30	† † †	† † †	29.3 50.0 51.6	0.2 0.2 0.2	63 18 20	† † †	† † †
Nitto-Denko Osaka, Japan	NTR-7250 NTR-7410¶ NTR-7450¶	PVA SPS SPES	Negative Negative Negative	62.5 500 92.0	0.2 0.5 0.5	50 10 50	0.2 0.5 0.5	98 9 32
Osmonics Minnetonkia, MN	B-type TLC¶	†	Negative	47.2	0.2	50	0.2	25
PCI England	AFC-30	PA	Negative	25.00	0.2	35	0.2	97
Toray Japan	SC-L100 UTC-20HF UTC-60	CA PA PA	Neutral Negative Amphoteric	31.3 94.7 47.3	0.2 0.2 0.1	75 66 85	0.2 0.2 0.2	97 99 99
UOP San Diego, CA	TFCS-4921 ROGA-4231	† †	† †	340 330	0.05 0.2	85 75	† †	95 95

* CA = cellulose acetate; PA = polyamide; PVA = polyvinyl alcohol; SPS = sulfonated polysulfone; SPES = sulfonated polyethersulfone.
† Data not available.
¶ These membranes show lower $MgSO_4$ rejections compared to other NF membranes; however, they have greater than 90% rejection of Na_2SO_4.

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negative. Thus, the concentration of a salt can be above that in the feed.

Since most NF membranes contain negatively charged hydrophilic groups attached to a hydrophobic UF support membrane, they have higher water fluxes than do RO membranes. This is due to the favorable orientation of water dipoles. Due to the surface active groups, they also have improved fouling resistance against hydrophobic colloids, oils, proteins, and other organics. This makes NF competitive with RO in high-fouling applications such as dye concentration and paper-waste treatment.

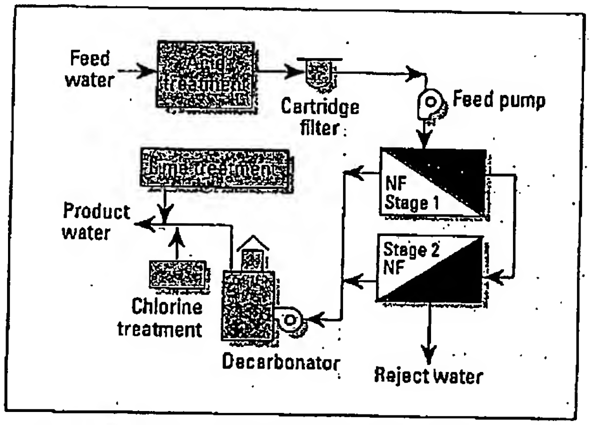
However, solutes with a charge opposite to that of the membrane interact with it, causing fouling. NF membranes are best in applications that reject uncharged molecules due to size exclusion and charged components due to electrostatic interaction. To illustrate the effectiveness of NF, some commercial applications are presented.

Demineralizing water

To date, the largest application of NF membranes is removing hardness and dissolved organics from water. Water hardness is caused by sulfate and bicarbonate salts of calcium and magnesium. Figure 3 shows a typical process for NF softening. Since the membranes are fouled by silicates, manganese, and iron, the feedwater is usually pretreated by acid to precipitate these dissolved salts, which are trapped by a cartridge filter.

The water is then sent to the first of two NF stages. The permeates from Stages 1 and 2 are the purified water streams. The retentate from Stage 2, containing most of the sulfates and bicarbonates, is discarded. The permeate streams can be further treated with chlorine to produce potable water. When operated at 0.5–0.7 MPa (70-100 psi), NF membranes reject 85–95% of the hardness and over 70% of the monovalent ions (*1*).

With its lower operating pressure, NF has lower operating costs and allows for some savings in pumps and piping, compared with RO. The pressurized water passes through energy-recovery turbines having an efficiency of 0.7, cutting energy consumption by 13% under that of an equivalent RO plant (*2,3*). Operation and maintenance costs are almost the same. However, the higher cost of NF membranes has so far offset these cost advantages.



■ *Figure 3. Water softening remains the largest use for NF plant. Adapted from (1).*

Cleaning up contaminated groundwater

Groundwater is often contaminated with organics from industrial effluents and agricultural runoff. In combination with chlorine, these organic contaminants form trihalomethanes (THMs) which are believed to be carcinogenic. NF membranes effectively remove these organics (*4–6*). In Palm Beach County, FL, NF membranes removed 97% of the total organic halogens and over 90% of total organic carbon (TOC) in potable water.

A study proved that a combination of slow sand filtration and NF is effective for secondary treated wastewater (*7*). The slow sand filter pretreatment reduces organic scaling on the NF membrane, while the NF membrane reduces salinity and hardness nitrates, heavy metals and other pollutants, color levels, and large amounts of dissolved organics. Simultaneously, THM formation is reduced. In this study, NF proved more energy-efficient than RO.

Ultrapure water

Ultrapure water is required in the electronics and semiconductor industries, in biotechnology, and in some medical applications. The water should be free of particles, debris of dead bacterial cells, and have a TOC of less than 5 ppb. Ion exchange can only achieve about 30 ppb TOC, most of which is composed of low-molecular-weight carbon compounds coming off of the ion-exchange resin. A negatively charged membrane with a low contact angle should give the best TOC reduction (*8*). NF membranes fit this description and can be used as a part of a larger system in the final polishing stage after ion exchange. To achieve the desired level of TOC content, however, more than one NF polishing stage is needed. The membranes can contribute to the TOC since they are made of polymers.

Effluents containing heavy metals

Rinse waters of many metalworking and allied industries contain significant amounts of heavy metals such as nickel, iron, copper, and zinc. To meet disposal regulations, these metals are removed by precipitating them out of waste streams as hydroxides. NF can clean up these streams, recovering up to 90% of the effluent as pure water, while simultaneously concentrating the heavy metals tenfold. The recovered metals can be reused (*6*).

Under the proper conditions, metals in a solution can also be separated

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